

10/574052**IAP5 Rec'd PCT/PTO 29 MAR 2006****METHOD FOR COLLAPSING MICROBUBBLES****TECHNICAL FIELD**

The present invention relates to a method of collapsing microbubble (microbubbles) that is useful in all technical fields, particularly in the technical field of water processing.

BACKGROUND ART

Bubbles having a diameter of 50 μm or less (microbubbles) are known to have properties different from those of normal bubbles, but the properties of the microbubbles are yet to be understood. For that reason, various microbubble generators under development recently only generate microbubble of a gas in aqueous solution, and there is almost no invention that makes the most of the potential properties of microbubbles. An example of the traditional technology using microbubbles is the method described in JP-A-2002-143885 of accelerating the biological activity, metabolism, and consequently growth of organisms. However, although the invention has significant advantageous in the field of cultivation of fish and shellfish, it does not disclose or suggest anything about collapsing microbubbles.

An example of the technology using the collapsing phenomenon of bubbles is a method of irradiating ultrasonic wave on bubbles. However, the method is extremely lower in efficiency because the bubbles for collapsing are generated by cavitation action of the ultrasonic wave itself, and has a problem of

difficulty in commercialization because of its restricted functions. Most of the cavitation bubbles generated then contain steam therein and the bubbles are present only for an extremely limited period of microseconds, and thus, the method had a problem that it was not possible to use the effects of the gas present in bubbles and the electric charge formed at the gas-liquid interface collapsing bubbles.

SUMMARY OF THE INVENTION

An object of the present invention, which was made in view of the circumstances described above, is to provide a method for collapsing microbubbles, physical and chemical actions obtained by collapsing microbubbles, a method for collapsing the microbubbles by discharge, a method for collapsing the microbubbles by ultrasonic wave, a method for collapsing the microbubbles by swirling current, a method for collapsing the microbubbles by using positive or negative pressure, and a method for collapsing the microbubbles by using the catalytic reaction of an oxidizer, as well as a method of decomposing microbes, viruses and the like, which were considered to be impossible by traditional technology.

The object of the present invention is accomplished by a method for collapsing microbubbles, characterized in that, in the step of the microbubbles having a diameter of 50 μm or less floated in a solution decreasing gradually by natural dissolution of the gas contained in the microbubbles and

disappearing finally, the microbubbles are disappeared by accelerating the speed of the microbubble size decrease by applying a stimulation to the microbubbles.

The object of the present invention is also accomplished more effectively by forming an ultrahigh-pressure ultrahigh-temperature region inside in an adiabatic compression-like change of the microbubbles caused by decrease of the microbubbles size; the electric charge density at the interface of the microbubbles increases rapidly and a great amount of free radical species are released from the gas-liquid interface; free radical species such as active oxygen species for decomposition of the substances present inside the microbubbles or in the area surrounding the microbubbles are generated by collapsing the microbubbles; the method gives rise to a compositional change of the chemical substances dissolved or floated in the solution; or the method sterilizes microorganisms such as microbes, viruses, and others present in the solution.

Further, the object of the present invention is also accomplished more effectively by applying the stimulation is electric discharge in a container containing a microbubble-containing solution generated by using a discharger; the stimulation is ultrasonic wave irradiated into a container containing a microbubble-containing solution by an ultrasonicator; or the ultrasonicator is connected to the container between a microbubble-containing solution outlet port

of a microbubble generator connected to container and an intake of the microbubble generator and the stimulation is given by continuous irradiation of ultrasonic wave into the container by the ultrasonicator.

When a circulation pipe is connected to a container containing a microbubble-containing solution, the object of the present invention is also accomplished more effectively by applying the stimulation is compression, expansion and swirling current generated by circulating part of the microbubble-containing solution in the container by the circulation pump and making the solution path through an orifice or porous plate having a single or multiple holes installed in the circulation pipe; the circulation pump gives a positive pressure of 0.1 MPa or more to the discharge side; the circulation pump gives a negative pressure lower than the environmental pressure to the intake side; or when a circulation pipe is connected to the container containing a microbubble-containing solution, the stimulation is compression, expansion and swirling current generated by feeding the microbubble-containing solution in the container into the circulation pipe and making the solution path through an orifice or porous plate having a single or multiple holes installed in the circulation pipe.

The object of the present invention is achieved more effectively by applying the the stimulation is forcibly internal circulation, in the pipe for feeding the microbubble-containing solution generated by a microbubble generator to a container,

of making the microbubble-containing solution discharged from the microbubble generator pass through a punching plate installed in the pipe, taken in part of the microbubble-containing solution from an intake installed between the punching plate and the container and feeding it into a pump, feeding the microbubble-containing solution into the pump, discharging it from an outlet port installed between the microbubble generator and the punching plate, and making it pass through the punching plate once again; or the pump gives a positive pressure of 0.1 MPa or more to the discharge side; the pump gives a negative pressure lower than the environmental pressure in the upstream pipe; the stimulation is a catalytic reaction generated by allowing an oxidant to react in the presence of a catalyst; the catalyst is copper and the oxidizer is ozone or hydrogen peroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing the results of measuring the zeta potential of microbubbles in distilled water.

Figure 2 is a diagram showing the electrification mechanism of microbubbles in water.

Figure 3 is a graph showing the relationship between the time period until microbubbles decrease of the microbubble size and disappear and the bubble diameter of the microbubbles.

Figure 4 is a graph showing the increase in zeta potential associated with decrease of microbubbles size.

Figure 5 is a side view of an apparatus for collapsing

the microbubbles by using a discharger.

Figure 6 is a side view of an apparatus for collapsing the microbubbles by using an ultrasonicator.

Figure 7 is a side view of an apparatus for collapsing the microbubbles by using swirling current.

Figure 8 is a side view of an apparatus for collapsing the microbubbles by using positive or negative pressure.

Figure 9 is a partial side view of the apparatus for collapsing the microbubbles by using positive or negative pressure.

Figure 10 is a side view of an apparatus for collapsing the microbubbles in the reaction of an oxidizer in the presence of a catalyst.

Figure 11 is an ESR spectrum of the free radicals generated during collapsing the microbubbles.

EXPLANATION OF NUMERALS

1 Container

2 Discharger

21 Anode

22 Cathode

3 Microbubble generator

31 Intake

32 Microbubble-containing solution outlet

4 Ultrasonicator

5 Circulation pump

- 6 Orifice (porous plate)
- 7 Oxidizer-supplying unit
- 8 Catalyst
- 9 Pump
- 10 Punching plate
- 11 Intake
- 12 Outlet

BEST MODE OF CARRYING OUT THE INVENTION

As shown in Figure 1, as a physical property of microbubbles, microbubbles in distilled water have an electric potential of approximately -30 to -50 mV independently of the diameter of bubbles. Thus, for example in water, as shown in Figure 2, a microbubble has a structure in which the bubble surface is surrounded by negative ions such as of OH^- , which in turn are surrounded additionally by cations such as of H^+ (H_3O^+).

In addition, a microbubble has a greater specific surface and a higher internal pressure than a normal bubble, because the surface tension acts more effectively. It is generally accepted academically that the internal pressure of a microbubble reaches as high as thousands of atmospheric pressures when it disappears.

Microbubbles are known to be normally lower rate of climb than normal bubbles and superior in gas dissolving capacity (natural dissolution). Thus, normal bubbles, when generated in water, rising toward the liquid surface direction and burst

at the liquid surface, while microbubbles rising more slowly than normal bubbles and have a superior dissolving capacity, thus resulting in gradual decrease in the bubble diameter and finally disappearance of the bubbles. Figure 3 shows the results of measuring the time until the microbubble decreases of its size and finally disappears. The microbubble having a smaller bubble diameter shows a shorter time of decrease of microbubble size and disappearance of the microbubble by natural dissolution. The maximum driving force for dissolving the gas in microbubbles is the self-compression effect by surface tension. The pressure buildup inside the microbubble with respect to environmental pressure can be estimated by the Young-Laplace's Formula.

(Formula 1)

$$\Delta P = 4\sigma/D$$

In the Formula, ΔP represents the degree of pressure buildup; σ , surface tension, and D , bubble diameter. In distilled water at room temperature, the pressure buildup is approximately 0.3 atmospheric pressure in a microbubble having a diameter of 10 μm and approximately 3 atmospheric pressures in the bubble having a diameter of 1 μm . The gas in a self-compressed bubble, which behaves in water according to the Henry's law in gas phase, dissolves efficiently in ambient water.

On the other hand, the speed of the microbubble size decrease by natural dissolution rises by application of a physical stimulation such as discharge, ultrasonic wave, or swirling current to the microbubble, and thus, the microbubble

is adiabatic compression and disappears (collapsing).

Adiabatic compression of the microbubble then gives rise to an extreme reaction field at ultrahigh temperature and ultrahigh pressure when the microbubble disappears.

As described above, a bubble present in water is charged negatively, but there are saturated electric charges formed at the gas-liquid interface according to environmental conditions such as pH, which can be observed by the zeta potential of the microbubble. The electric charges not due to electrolytic ions and others in water, but are based on the structural factor of water itself. That is, the electric charges are generated by interfacial adsorption of OH^- and H^+ ions, based on the difference between the hydrogen-bonded network structure at the gas-liquid interface and the structure of bulk. The structure formed also has an action to suppress thermal molecular movement, and thus, it takes time of about several seconds to go back to the equilibrium condition after the electric charge density fluctuates

Decrease of the bubble size by natural dissolution of the microbubble is accompanied with decrease in the surface area of gas-liquid interface. The surface area of the gas-liquid interface decreases more rapidly as the bubble becomes smaller, as shown in Figure 3. When the speed of the decrease in the surface area of gas-liquid interface is lower, the electric charge density at the gas-liquid interface remains in the condition almost in equilibrium. However, as shown in Figure 4, when the bubble diameter decreases to 10 μm or less, dissipation

of electric charge cannot catch up the speed of the size decrease, which is observed as an increase in zeta potential associated with deviation from equilibrium. However, the decrease in the surface area of gas-liquid interface by natural dissolution is not so rapid, and the value of electric charge density remains up to several times larger than that in equilibrium, even at the point immediately before disappearance.

In contrast, during the collapsing microbubbles according to the present invention, the speed of the decrease in the surface area of gas-liquid interface is very high, and the electric charge remains as it is without dissipation and deviates from equilibrium, resulting in generation of a region extremely higher in electric charge density. When the bubble having a diameter of 20 μm decreases into the microbubble of 0.5 μm or less by collapsing, the electric charge density rises to a value as high as 1,000 times larger than that in equilibrium.

The extremely high-density electric charge formed by collapsing is in a non-equilibrium condition and extremely instable, and the system returns back to a stable state in a phenomenon different from simple dissipation. Thus, an extremely large potential gradient is formed between the bubble interface and its surrounding area in the collapsing process, and the equilibrium of the electric charge condition is reestablished by electron transfer, for example, by discharge.

It means generation of an extremely high-density energy field, and when the collapsing is performed in water, it is

accompanied with generation of free radical species by decomposition of ambient water molecules. In addition, because the electric charge carriers are OH^- and H^+ , free radical species such as $\cdot\text{OH}$ and $\cdot\text{H}$ are formed by neutralization of electric charges by discharge.

The free radical species, which are very highly reactive, react with various compounds dissolved or suspended in solution, changing composition or decomposing the compounds in solution. Because an extreme reaction field at ultrahigh temperature and ultrahigh pressure is formed during collapsing, it becomes possible to sterilize microorganisms such as microbes and viruses and decompose aromatic compounds such as phenol, although it was hitherto regarded as impossible. Examples of the substances decomposed by collapsing include almost all organic compounds, inorganic compounds such as FeSO_4 , CuNO_3 , AgNO_3 , and MnO_2 ; dioxins, PCBs, chlorofluorocarbons, microbes, viruses, and the like.

Hereinafter, the method for collapsing the microbubbles will be described.

Figure 5 is a side view illustrating an apparatus for collapsing the microbubbles by discharge. The microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas is injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container

1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. An anode 21 and a cathode 22 are placed in the container 1, and the anode 21 and the cathode 22 are connected to a discharger 2.

First, microbubbles are generated in the container 1 containing a solution by using the microbubble generator 3. The solution in the container 1 used for generation of microbubbles is preferably water (distilled water, tap water, or the like), seawater, or the like; but an organic solvent such as oil, alcohol, acetone, toluene, or petroleum oil may also be used. In the present specification, water is used as the solution for convenience in description, but the present invention is not limited thereto.

The solution is discharged in the container 1 by using the discharger 2. A saturation bubble concentration of microbubbles in the container 1 is preferably 50% or more, for more effective collapsing during the underwater discharge. In addition, the voltage of the underwater discharge is preferably 2,000 to 3,000 V. The stimulation of underwater discharge raises the speed of microbubble size decrease by natural dissolution of the microbubbles in water and results in collapsing (disappearance) the bubbles. Extreme reaction fields are formed and free radicals such as $\cdot\text{OH}$ and $\cdot\text{H}$ are formed by decomposition of water, simultaneously with disappearance of microbubbles, and the substances and others present in water are decomposed.

The gas used for generation of microbubbles in the microbubble generator 3 is not particularly limited, and may be; or alternatively, the microbubbles may be generated with ozone or oxygen. Microbubbles generated with oxygen or ozone higher in oxidative potential results in generation of a greater number of free radical species during collapsing, and give an action to decompose hazardous substances and others superior both in the quantitative and qualitative points as well as a sterilizing action. Alternatively, the microbubbles may be generated after oxygen or ozone is previously contained in the solution in the container.

Hereinafter, a method for collapsing the microbubbles by ultrasonication will be described. Description on the devices the same as those described in the method for collapsing the microbubbles by discharge will be omitted.

Figure 6 is a side view illustrating an apparatus for collapsing the microbubbles by ultrasonic wave. A microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. An ultrasonicator 4 is installed on the container 1. The

installation site of the ultrasonicator 4 is not particularly limited, but preferably between the intake 31 and the microbubble-containing solution outlet 32, for more efficient collapsing the microbubbles.

Microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

Then, ultrasonic wave is irradiated on the microbubble-containing water in the container 1 by using the ultrasonicator 4. During collapsing the microbubbles by ultrasonic wave irradiation, the saturation bubble concentration of microbubbles in the container 1 is preferably 50% or more, for more effective collapsing the microbubbles. Ultrasonic wave irradiation at a saturation bubble concentration of 50% or more leads to more efficient collapsing. The irradiation frequency of the ultrasonic wave is preferably 20 kHz to 1 MHz; and the exposure time of ultrasonic wave is preferably 30 seconds or less, but the irradiation may be continued for an extended period of time.

In the conventional methods of destructing hazardous substances and others by ultrasonic wave, which were simple irradiation of ultrasonic wave on normal water, lower in the efficiency of generating free radicals by collapsing, and thus had an insufficient action, it was not possible to decompose aromatic compounds such as phenol; but it became possible to destruct microbes, viruses, and aromatic compounds such as phenol, which were not possible hitherto, by collapsing the microbubbles

by irradiating ultrasonic wave on the microbubbles as in the present invention.

Hereinafter, a method for collapsing the microbubbles by swirling current will be described. Description on the devices the same as those in the method for collapsing the microbubbles by discharge pressure and the method for collapsing the microbubbles by ultrasonication will be omitted.

Figure 7 is a side view illustrating an apparatus for collapsing the microbubbles by swirling current. A microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way, microbubbles are generated in the container 1. A circulation pump 5 is connected to the container 1 for partial circulation of the microbubble-containing solution in the container 1, and an orifice having multiple holes (porous plate) 6 is placed in the pipe (circulation pipe) which is connected to the circulation pump 5 at one end and to the container 1 at the other end. Part of the microbubble-containing solution poured out of the circulation pipe is re-circulated by the circulation pump and an swirling current is formed during passage through the orifice (porous plate) 6.

First, microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

The microbubble-containing water is then fed into the circulation pump 5 for partial circulation. The microbubble-containing water is further fed by the circulation pump 5 to the orifice (porous plate) 6, and an swirling current is formed in the pipe downstream thereof. The microbubbles are crushed by expansion or compression of the microbubbles during passage and by the electric swirling current generated by the swirl of electrically charged microbubbles due to the swirling current generated in the pipe. The positions of the circulation pump 5 and the orifice (porous plate) 6 on the channel may be altered.

Although only one orifice (porous plate) 6 is shown in Figure 7, multiple orifices may be installed, and the circulation pump 5 may be eliminated as needed. Alternatively, the orifice 6 may be replaced with a punching plate. When a circulation pump 5 is installed, the pressure (positive pressure) of compressing the solution toward the orifice (porous plate) 6 is preferably 0.1 MPa or more. A positive pressure of less than 0.1 MPa may lead to insufficient eddy current generation. In addition, the pump 5 gives a negative pressure lower than the environmental pressure in the upstream pipe.

Figure 8 is a side view illustrating a method for collapsing by using positive or negative pressure; and Figure 9 is a partially magnified drawing of the area of a punching plate 10 and a pump

9 (the arrow in Figure 9 indicates the direction of the flow of microbubble-containing solution). Description on the devices the same as those described above will be omitted.

As shown in Figure 8, it is an apparatus for collapsing of microbubbles by draining the microbubble-containing water discharged from a microbubble generator 3 through a punching plate 10. The punching plate 10 is placed between two microbubble-containing solution outlets 32 (between the container 1 and the microbubble generator 3). An intake 11 for compressing the microbubble-containing solution to a pump 9 is formed between the punching plate 10 and the container 1 in the microbubble-containing solution outlet 32. Part of the microbubble-containing solution taken in into the intake 11 is fed to the pump 9 and then further forward by the pressure of the pump 9. The microbubble-containing solution is fed by the pump 9 via an outlet port 12 formed between the microbubble generator 3 and the punching plate 10 into the microbubble-containing solution outlet 32, and passes through the punching plate 10 once again. Thus, it is possible to crush the microbubbles by performing internal circulation forcibly by the pump 9 and increasing the swirling current drastically during passage through the punching plate 10. The positive pressure of the pump 9 is preferably adjusted to 0.1 MPa or more for forcibly internal circulation of the microbubble-containing solution in the microbubble-containing solution outlet 32. A positive pressure of pump 9 of less than 0.1 MPa results in

inefficient internal circulation. The pump 9 also give a negative pressure lower than the environmental pressure in the intake side (intake 11). The positive pressure is a pressure higher than the environmental pressure, i.e., a pressure of the pump 9 feeding the solution, while the negative pressure is a pressure lower than the environmental pressure, i.e., a pressure generated when the pump 9 takes in the solution.

Multiple punching plates 10 may be installed according to application, and multiple pumps 9 may be installed as needed in the method for collapsing the microbubbles shown in Figures 8 and 9. In addition, for example, a check valve may be installed in the microbubble-containing solution outlet 32 as needed.

Hereinafter, a method for collapsing the microbubbles by using the catalytic action of an oxidizer during its reaction. Description on the devices the same as those described above will be omitted.

Figure 10 is a side view illustrating an apparatus for collapsing the microbubbles by using the catalytic action of an oxidizer during its reaction. A microbubble generator 3 takes in the solution in a container 1 through an intake 31; a gas injected into the microbubble generator 3 through an injection port (not shown in the Figure) for injecting a gas for generating microbubble and mixed with the solution taken in through the intake 31; and the microbubbles generated in the microbubble generator 3 are fed back into the container 1 through a microbubble-containing solution outlet 32. In this way,

microbubbles are generated in the container 1. An oxidizer-supplying unit 7 is connected to the container 1, and an oxidizer is supplied therefrom into the container 1.

Microbubbles are generated in the container 1 containing water by using the microbubble generator 3.

Then, a catalyst is added to the container 1. Favorable examples of the catalysts include various catalysts known in the art, including metal catalysts such as copper, palladium, iron, vanadium, tin, titanium, zirconium, platinum, manganese, cobalt, nickel, rubidium, rhodium, and zinc; these catalysts may be used alone or in combination of two or more; and copper is more preferable. The microbubbles may be generated after addition of the catalyst into the container 1.

An oxidizer is supplied from the oxidizer-supplying unit 7. The oxidizer is not particularly limited, and any one of various known oxidizers such as ozone, hydrogen peroxide, sodium hypochlorite, manganese dioxide, sulfuric acid, nitric acid, potassium permanganate, copper chloride, and silver oxide may be used favorably; these oxidizers may be used alone or in combination of two or more; and in particular, ozone and hydrogen peroxide are more preferable.

Supply of an oxidizer into the container 1 results in generation of very high oxidative radicals in the reaction between the oxidizer and the catalyst. The radicals accelerate collapsing the microbubbles by their collision to the microbubbles. Although it is possible to decompose hazardous

substances contained in water in the reaction between the oxidizer and the catalyst, it became possible to decompose hazardous substances more efficiently and also to decompose and sterilize microorganisms such as microbes and viruses, by the collapsing the microbubbles by using the catalytic action associated with the reaction between the oxidizer and the catalyst.

Hereinafter, the methods for collapsing the microbubbles will be described with reference to Examples, but it should be understood that the present invention is not restricted thereby.

EXAMPLES

Example 1

10 L of phenol-containing water was placed in the container 1 shown in Figure 5. Microbubbles are generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. The microbubbles were formed continuously, while the saturation bubble concentration of microbubbles in the container is controlled to 1 to 50% or more.

Then, the water was electrically discharged at a voltage of 2,400 V ten times per 10 minutes by the discharger 2, for collapsing the microbubbles.

Analysis of the water during collapsing by ESR gave the spectrum shown in Figure 11, confirming the presence of free

radical species therein. The ESR spectrum shown in Figure 11 is determined, as a spin-trapping agent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) is added to the sample. The results demonstrated generation of free radicals.

After the collapsing the microbubbles, phenol had been decomposed completely.

Example 2

10 L of phenol-containing water was placed in the container 1 shown in Figure 6. Microbubbles are generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the saturation bubble concentration of microbubbles in the container was controlled to 1 to 50% or more.

Then, the microbubbles are crushed by irradiation of an ultrasonic wave at an irradiation frequency of 200 kHz by the ultrasonicator 4 for 10 minutes. ESR spectral analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol had been decomposed completely after the collapsing the microbubbles.

Example 3

10 L of phenol-containing water was placed in the container

1 shown in Figure 7. Microbubbles are generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container 1, to give microbubble-containing water. Microbubbles were formed continuously, while the saturation bubble concentration of microbubbles in the container was controlled to 1 to 50% or more.

Then, the microbubble-containing water in the container 1 was circulated partially, and part of the microbubble-containing water was introduced into the circulation pipe connected to the circulation pump 5. The microbubble-containing water introduced into the circulation pump 5 was fed to the orifice (porous plate) 6 at a positive pressure of 0.3 MPa, allowing the microbubbles crushed by the swirling current generated there.

ESR spectral analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol had been decomposed completely after the collapsing the microbubbles.

Example 4

10 L of phenol-containing water was placed in the container 1 shown in Figure 8. Microbubbles are generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container

1, to give microbubble-containing water. Microbubbles were formed continuously, while the saturation bubble concentration of microbubbles in the container was controlled to 1 to 50% or more.

Then, part of the microbubble-containing water discharged from the microbubble generator 3 and passing out of the punching plate 10 was taken in through the intake 11 by operation of the pump 9 and fed by the pump 9 to the discharge side, for forcibly internal circulation thereof in the microbubble-containing solution outlet 32. The positive pressure of the pump 9 then was 0.5 MPa. The microbubble-containing water fed by the pump 9 was made to pass through the punching plate 10 once again via the outlet port 12. Such an internal circulation raised the swirling-current efficiency drastically and was effective in collapsing the microbubbles.

ESR spectrum analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol had been decomposed completely after the collapsing the microbubbles.

Example 5

10 L of phenol-containing water was placed in the container 1 shown in Figure 10. Microbubbles are generated in the microbubble generator 3 by using ozone as the gas for preparation of microbubbles and supplied into the water in the container

1, to give microbubble-containing water. Microbubbles were formed continuously, while the saturation bubble concentration of microbubbles in the container was controlled to 1 to 50% or more.

Then, 5 g of a powdery copper catalyst was placed in the container 1, and an ozone gas was supplied from the oxidizer-supplying unit 7 into the container 1. The amount of the ozone gas supplied was 1 g. The microbubbles were crushed by the catalytic reaction associated with the reaction between the ozone gas and the copper catalyst when the ozone gas was supplied.

ESR spectrum analysis of the water during collapsing similar to that in Example 1 gave an ESR spectrum similar to that shown in Figure 11.

Phenol had been decomposed completely after the collapsing the microbubbles.

Advantageous effects of the invention

Collapsing the microbubbles by the method according to the present invention lead to increase in the speed of microbubbles size decrease due to utilization of a stimulation (discharge, ultrasonic wave, swirling current, positive and negative pressure, or the catalytic reaction associated with the reaction of oxidizer, or the like), disappearance of microbubbles and generation of active oxygen species and free radical species for decomposition of substances present inside

the microbubbles or in the area surrounding the microbubbles, and compositional change thereby of the chemical substances dissolved or floated in water; and thus, it became possible to sterilize microorganisms such as microbes, viruses, and others present in solution and decompose aromatic compounds such as phenol, which was difficult in the past, and thus, to decompose almost all hazardous substances and others.

Industrial applicability

By the collapsing the microbubbles according to the present invention, it became possible to sterilize microorganisms such as microbes, viruses, and others present in solution and decompose aromatic compounds such as phenol, which were difficult to decompose in the past, and the method is applicable in the fields for processing hazardous substances and the like.